

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 May 2001 (31.05.2001)

PCT

(10) International Publication Number
WO 01/38275 A1

(51) International Patent Classification: C07C 17/25,
21/04, 21/067, 21/073, 1/30

(21) International Application Number: PCT/US00/31488

(22) International Filing Date:
16 November 2000 (16.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/166,897 22 November 1999 (22.11.1999) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,
TZ, UA, UG, US, UZ, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/38275 A1

(54) Title: DEHYDROHALOGENATION OF HALOGENATED ALKANES USING RARE EARTH HALIDE OR OXYHALIDE CATALYST

(57) Abstract: A process for the dehydrohalogenation of halogenated alkanes involving contacting a halogenated alkane having three or more carbon atoms with a rare earth halide or rare earth oxyhalide catalyst under process conditions sufficient to prepare an alkene or halogenated alkene. The process converts low valued halogenated alkanes, which are by-products of industrial chlorination processes, into higher valued alkenes and halogenated alkenes. 1,2-Dichloropropane, for example, can be dehydrochlorinated predominantly to allyl chloride and 1-chloropropene with little production of low value 2-chloropropene. 1,2,3-Trichloropropane can be dehydrochlorinated predominantly to 1,3-dichloropropene which is useful in soil fumigants.

DEHYDROHALOGENATION OF HALOGENATED ALKANES
USING RARE EARTH HALIDE OR OXYHALIDE CATALYST

5 This application claims the benefit of U.S. Provisional Application No. 60/166,897,
filed November 22, 1999.

 This invention pertains to a process of catalytically dehydrohalogenating a
halogenated alkane, such as 1,2-dichloropropane or 1,2,3-trichloropropane, to produce an
10 alkene or a halogenated alkene, such as allyl chloride or 1,3-dichloropropene, respectively.

 Alkenes, such as propylene, find wide utility as monomers in the manufacture of
polyolefin polymers and synthetic rubbers. Halogenated alkenes find utility in a variety of
basic and specialty chemicals. Allyl chloride, for example, is a valuable starting material in
15 the preparation of epichlorohydrin, from which epoxy polymers are manufactured. 1,3-
Dichloropropene and other chlorinated alkenes find utility as components in nematocides,
soil fumigants, insecticides, and as monomers in the production of plastics, resins, and
chemical intermediates.

20 The manufacture of allyl chloride involves contacting propylene and chlorine rapidly
at elevated temperatures, as described, for example, in U.S. 4,319,062. The by-product
stream that is obtained as material of intermediate boiling point, after removing the lower
boiling fractions containing the allyl chloride and the higher boiling fractions containing
mostly cis- and trans-1,3-dichloropropenes by distillation, contains a variety of chlorinated
25 propanes and propenes including 1,2-dichloropropane, 3,3-dichloropropene, 2,3-
dichloropropene, 2,2-dichloropropane, and other related chlorinated C₃ species. Usually,
1,2-dichloropropane is present as a major component, often amounting to approximately 70
to 95 mole percent, and typically 75 to 90 mole percent, of the by-product stream. Usually
3,3-dichloropropene is present in an amount ranging from 0.1 to 15 mole percent of the by-
30 product stream. 3,3-Dichloropropene is typically isomerized to yield the above-mentioned
1,3-dichloropropene, as described, for example, in US 5,072,063 and 5,510,546. 1,2-
Dichloropropane is not useful *per se* and must also be up-graded to a product of higher
value.

Typically, 1,2-dichloropropane has been up-graded via thermal dehydrochlorination to allyl chloride. By-products of the thermal dehydrochlorination include cis- and trans-1-chloropropene, which can be recycled to the aforementioned allyl chloride manufacturing process, wherein propylene is chlorinated to allyl chloride. The chlorination therein of cis and trans-1-chloropropene produces 1,3-dichloropropene, a valuable chemical used in fumigant formulations, as indicated previously. A less favorable by-product of the thermal dehydrochlorination of 1,2-dichloropropane is 2-chloropropene, which cannot be readily used or up-graded to a product of higher value. It would be highly desirable to discover a dehydrohalogenation process which converts 1,2-dichloropropane principally to allyl chloride and 1-chloropropenes with essentially no formation, or at best a lower formation, of the less valuable 2-chloropropene.

As another example, allyl chloride product can itself be chlorinated to form 1,2,3-trichloropropane, a by-product of very limited value and utility; but 1,2,3-trichloropropane can be dehydrohalogenated to form 1,3-dichloropropene, which has utility in fumigants. Conventional dehydrohalogenation processes, however, typically produce unfavorable yields of 2,3-dichloropropene, which may be difficult to separate by simple distillation. It would be desirable to discover a dehydrohalogenation process that converts 1,2,3-trichloropropane to the more desirable cis and trans-1,3-dichloropropene products with reduced levels of 2,3-dichloropropene.

This invention is a novel process of dehydrohalogenating a halogenated alkane to form an alkene or a halogenated alkene. The novel process of this invention comprises contacting a halogenated alkane having three or more carbon atoms with a dehydrohalogenation catalyst under reaction conditions sufficient to produce the alkene or halogenated alkene. In the novel process of this invention, the dehydrohalogenation catalyst comprises a rare earth halide or rare earth oxyhalide compound.

The novel process of this invention simply and efficiently converts a halogenated alkane via dehydrohalogenation (cracking) in the presence of a rare earth halide or rare earth oxyhalide catalyst to an alkene or a halogenated alkene. The process of this invention can

be advantageously used to up-grade lower valued halogenated alkanes to higher valued alkenes or halogenated alkenes suitable for commercial use. As an example, 1,2-dichloropropane, produced in the chlorination of propylene to allyl chloride, can be advantageously dehydrohalogenated by the process of this invention to allyl chloride and 1-chloropropene in high yield. 2-Chloropropene, an undesirable by-product of the dehydrohalogenation of 1,2-dichloropropane, is produced at an advantageously low level in the process of this invention. 1-Chloropropene, produced in the cracking process herein of 1,2-dichloropropane, can be beneficially recycled to the allyl chloride reactor and chlorinated to 1,3-dichloropropene, which is useful in fumigants. As another example of the process of this invention, 1,2,3-trichloropropane can be beneficially dehydrohalogenated to produce predominantly 1,3-dichloropropene, having the aforementioned utility in fumigants. As a further advantage of this invention, typically the dehydrohalogenation occurs at a temperature that is lower than the temperatures required of prior art dehydrohalogenation processes. Accordingly, the process of this invention consumes less energy than prior art processes and provides the opportunity for higher conversion at lower operating temperatures. As yet another advantage, the rare earth halide catalyst of this invention is soluble in water. Accordingly, should process equipment, such as filters, transport lines, valves, and intricate small or curved parts of the reactor, become plugged with catalyst particles, the plugged parts need only be washed with water to restore the parts to working order.

In its broadest concept, this invention is a novel process comprising the catalytic dehydrohalogenation of a halogenated alkane to form an alkene or a halogenated alkene. The novel process of this invention comprises contacting a halogenated alkane having three or more carbon atoms with a dehydrohalogenation catalyst under reaction conditions sufficient to prepare the alkene or halogenated alkene. The dehydrohalogenation catalyst used in the novel process of this invention comprises a rare earth halide or rare earth oxyhalide compound.

In a preferred embodiment, this invention is a novel process comprising the catalytic dehydrochlorination of a chlorinated alkane so as to form an alkene or a chlorinated alkene. In this preferred embodiment, the novel process comprises contacting a chlorinated

alkane having three or more carbon atoms with a dehydro-chlorination catalyst under reaction conditions sufficient to prepare the corresponding alkene or chlorinated alkene, the dehydrochlorination catalyst being a rare earth halide or rare earth oxyhalide, more preferably, a rare earth chloride or rare earth oxychloride. In another more preferred embodiment, the chlorinated alkane is 1,2-dichloropropane or a mixture of chlorinated alkanes comprising predominantly 1,2-dichloropropane, and the halogenated alkene comprises allyl chloride, 1-chloropropene, or essentially a combination thereof. In another more preferred embodiment, the chlorinated alkane is 1,2,3-trichloropropane, and the halogenated alkene is 1,3-dichloropropene.

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The halogenated alkane, which is used in the process of this invention, can be any halogenated alkane having three or more carbon atoms. The halogenated alkane may also be an essentially pure halogenated alkane or a mixture of halogenated alkanes. Preferably, the halogenated alkane is a halogenated C_{3-8} alkane or mixture of halogenated C_{3-8} alkanes.

15 More preferably, the halogenated alkane is a halogenated C_{3-4} alkane or a mixture of halogenated C_{3-4} alkanes. The halogenated alkane will possess at least one halogen substituent. Full saturation with halogen substituents is typically not preferred. At least one hydrogen atom is preferably present on at least one of the carbon atoms, because the dehydrohalogenation proceeds by eliminating hydrogen halide from the halogenated alkane.

20 Each halogen substituent, which is present, may be independently selected from chlorine, bromine, and iodine substituents. Preferably, the halogen substituent is selected from chlorine or bromine substituents. Fluorine substituents may be present on the halogenated alkane; but typically fluorine remains inert and does not participate in dehydrofluorination (loss of HF). Non-limiting examples of suitable halogenated alkanes include 1,2-

25 dichloropropane, 1,2,3-trichloropropane, 1,2-dichlorobutane, 2,3-dichlorobutane, 1,2,3-trichlorobutane, 1,2-dibromopropane, 1,2,3-tribromopropane, 1,2-dibromobutane, 1,2,3-tribromobutane, as well as isomers and higher homologues of the aforementioned halogenated alkanes, and mixtures of any of the aforementioned compounds. The halogenated alkanes may be provided in mixtures which also contain halogenated alkenes.

30 Most preferably, the halogenated alkane is 1,2-dichloropropane or 1,2,3-trichloropropane.

In another most preferred embodiment, the halogenated alkane is a mixture of 1,2-dichloropropane with di- and tri-chlorinated C₃ alkanes and C₃ alkenes. These mixtures, known in the art as "allyl propylene dichloride" ("allyl PDC"), may be obtained as by-product streams in the chlorination of propylene to form allyl chloride. "Allyl PDC" compositions can vary with the specific conditions in the allyl chloride reactor and the particular purification steps employed. Purification steps can include distillation, isomerization, selective reaction, and other separation operations known to those skilled in the art. A typical "allyl PDC" composition comprises from 70 to 95 mole percent 1,2-dichloropropane, from 1 to 15 mole percent 2,3-dichloropropene, from 0.1 to 15 mole percent 3,3-dichloropropene, from 0.1 to 10 mole percent 1,3-dichloropropene isomers, from 0 to 3 mole percent 1,1-dichloropropene, and may contain other chlorinated alkanes and alkenes as well as non-chlorinated compounds.

Optionally, if desired, the feed to the dehydrohalogenation process comprising the halogenated alkane can be diluted with a diluent or carrier gas, which may be any gas that does not substantially interfere with the dehydrohalogenation process. The diluent may assist in removing products and heat from the reactor and in reducing the number of undesirable side-reactions. Non-limiting examples of suitable diluents include nitrogen, argon, helium, carbon monoxide, carbon dioxide, steam, condensable halogenated hydrocarbons, and mixtures thereof. For the purposes of this invention, the term "condensable halogenated hydrocarbons" will include any halogenated hydrocarbon which is substantially inert with respect to the dehydrohalogenation process of this invention and which is readily separated from the dehydrohalogenation product effluent by fractional distillation or cooling. Fully perhalogenated alkenes, such as perchloroethylene and perfluoroethylene, may be suitably employed as the condensable halogenated hydrocarbon. The quantity of diluent employed typically ranges from greater than 10 mole percent, and preferably, greater than 20 mole percent, to typically, less than 90 mole percent, and preferably, less than 70 mole percent, based on the total moles of starting halogenated alkane and optional diluent.

One catalyst which is employed in the novel dehydrohalogenation process of this invention comprises a rare earth halide. The rare earths are a group of 17 elements

consisting of scandium (atomic number 21), yttrium (atomic number 39) and the lanthanides (atomic numbers 57-71) [James B. Hedrick, U.S. Geological Survey - Minerals Information - 1997, "Rare-Earth Metals"]. Preferably, herein, the term is taken to mean an element selected from lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof. Preferred rare earth elements for use in the aforementioned dehydrohalogenation process are those which are typically considered as being single valency metals. Catalytic performance of multi-valency metals appears to be less desirable than those that are single valency. The rare earth element for this invention is even more preferably selected from lanthanum, neodymium, praseodymium, and mixtures thereof. Most preferably, the rare earth element used in the catalyst is lanthanum or a mixture of lanthanum with other rare earth elements.

Preferably, the rare earth halide is represented by the formula MX_3 wherein M is at least one rare earth element selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is chloride, bromide, or iodide. More preferably, X is chloride, and the more preferred rare earth halide is represented by the formula MCl_3 , wherein M is defined hereinbefore. Most preferably, X is chloride and M is lanthanum, and the rare earth halide is lanthanum chloride, which optionally can be mixed with other rare earth chlorides.

In an alternative embodiment, the rare earth halide catalyst is porous, which means that the catalyst contains void spaces, such as channels, pores, and/or cavities, within its crystallographic structure. This porosity creates surface area throughout the compound. Typically, the porous rare earth halide has a BET surface area greater than $5 \text{ m}^2/\text{g}$, as determined by the BET (Brunauer-Emmett-Teller) method of measuring surface area, described by S. Brunauer, P. H. Emmett, and E. Teller, *Journal of the American Chemical Society*, 60, 309 (1938). Preferably, the porous rare earth halide has a BET surface area greater than $10 \text{ m}^2/\text{g}$, more preferably, greater than $15 \text{ m}^2/\text{g}$, even more preferably, greater than $20 \text{ m}^2/\text{g}$, and most preferably, greater than $30 \text{ m}^2/\text{g}$. For these above measurements, the

nitrogen adsorption isotherm is measured at 77K, and the surface area is calculated from the isotherm data utilizing the BET method.

In another aspect, the catalyst of this novel dehydrohalogenation process comprises a rare earth oxyhalide, the rare earths being identified hereinbefore. Preferably, this form of the catalyst is represented by the formula MOX , wherein M is at least one rare earth element selected from the group consisting of lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, lutetium, and mixtures thereof; and wherein X is selected from the group consisting of chloride, bromide, and iodide. More preferably, the rare earth oxyhalide is a rare earth oxychloride, represented by the formula $MOCl$, wherein M is defined hereinbefore. Most preferably, the rare earth oxychloride is lanthanum oxychloride, $LaOCl$, optionally mixed with other rare earth oxychlorides.

In an alternative embodiment, the rare earth oxyhalide is porous, as defined hereinbefore in connection with the rare earth halide. Typically, the porous rare earth oxyhalide has a BET surface area of greater than $12 \text{ m}^2/\text{g}$, preferably, greater than $15 \text{ m}^2/\text{g}$, more preferably, greater than $20 \text{ m}^2/\text{g}$, and most preferably, greater than $30 \text{ m}^2/\text{g}$. Generally, the BET surface area is less than $200 \text{ m}^2/\text{g}$. In addition, it is noted that the $MOCl$ phases possess characteristic powder X-Ray Diffraction (XRD) patterns that are distinct from the MCl_3 phases.

It may also be advantageous to include other elements within the catalyst. For example, preferable elemental additives include alkali and alkaline earths, boron, phosphorous, sulfur, germanium, titanium, zirconium, hafnium, the noble metals, and combinations thereof. The noble metals include ruthenium, rhodium, palladium, osmium, iridium, platinum, silver, and gold. These elements can be present to alter the catalytic performance of the composition or to improve the mechanical properties (for example, attrition-resistance) of the material. The total concentration of elemental additives in the catalyst is typically greater than 0.01 weight percent and typically less than 20 weight percent, based on the total weight of the catalyst.

In the discussion hereinabove, the catalysts are not bound to a support or carrier. In an alternative embodiment, the rare earth halide or rare earth oxyhalide catalyst may be bound to, extruded with, or deposited onto a catalyst support or carrier. Non-limiting examples of suitable carriers include alumina, silica, silica-alumina, porous aluminosilicate (zeolite), silica-magnesia, bauxite, magnesia, silicon carbide, titanium oxide, zirconium oxide, zirconium silicate, or combinations thereof. In this supported embodiment, the support is used in a quantity greater than 1 weight percent, and preferably, greater than 10 weight percent, based on the total weight of the catalyst and support. In this supported embodiment, the support is used in a quantity less than 90 weight percent, preferably, less than 80 weight percent, and more preferably, less than 70 weight percent, based on the total weight of the catalyst and support.

The rare earth halide and rare earth oxyhalide catalysts may be obtained from commercial suppliers. The porous rare earth halide and porous rare earth oxyhalide catalysts may be synthesized as described hereinafter, as the porous embodiments of the catalyst are not known to be commercially available at the current time.

A method currently felt to be preferable for forming the composition comprising the porous rare earth oxyhalide (MOX) comprises the following steps: (a) preparing a solution of a halide salt of the rare earth element or elements in a solvent comprising either water, an alcohol, or mixtures thereof; (b) adding a base to cause the formation of a precipitate; and (c) collecting and calcining the precipitate in order to form the MOX. Preferably, the halide salt is a rare earth chloride salt, for example, any of such salts which are commercially available. Typically, a nitrogen-containing base is employed selected from ammonium hydroxide, alkyl amines, aryl amines, arylalkyl amines, alkyl ammonium hydroxides, aryl ammonium hydroxides, arylalkyl ammonium hydroxides, and mixtures thereof. The nitrogen-containing base may also be provided as a mixture of a nitrogen-containing base with other bases that do not contain nitrogen. Preferably, the nitrogen-containing base is ammonium hydroxide or tetra(alkyl)ammonium hydroxide, more preferably, tetra(C₁₋₂₀ alkyl)ammonium hydroxide. The solvent in Step (a) is preferably water. Porous rare earth oxychlorides may also be produced by appropriate use of alkali or alkaline earth hydroxides, preferably, with the buffering action of a nitrogen-containing base. Generally, the

precipitation is conducted at a temperature greater than 0°C. Generally, the precipitation is conducted at a temperature less than 200°C, preferably, less than 100°C. The precipitation is conducted generally at ambient atmospheric pressure, although higher pressures may be used, as necessary, to maintain liquid phase at the precipitation temperature employed. The calcination is typically conducted at a temperature greater than 200°C, preferably, greater than 300°C, but less than 800°C, and preferably, less than 600°C. Mixtures of carboxylic acid and rare earth chloride salts also can yield rare earth oxychlorides upon appropriate decomposition.

10 A method currently felt to be preferable for forming the catalyst composition comprising the porous rare earth halide (MX_3) comprises the following steps: (a) preparing a solution of a halide salt of the rare earth element or elements in a solvent comprising either water, an alcohol, or mixtures thereof; (b) adding a base to cause the formation of a precipitate; (c) collecting and calcining the precipitate; and (d) contacting the calcined
15 precipitate with a halogen source. Preferably, the rare earth halide is a rare earth chloride salt, such as any commercially available rare earth chloride. Preferably, the solvent is water, and the base is any of those bases noted hereinbefore in connection with the preparation of MOX. Likewise, the precipitation is generally conducted at a temperature greater than 0°C and less than 200°C, preferably less than 100°C, at ambient atmospheric pressure or a higher
20 pressure so as to maintain liquid phase. The calcination is typically conducted at a temperature greater than 200°C, preferably, greater than 300°C, but less than 800°C, and preferably, less than 600°C. Preferably, the halogen source is a halogen halide, such as hydrogen chloride, hydrogen bromide, or hydrogen iodide, or is a molecular halogen, such as molecular chlorine, bromine, or iodine. More preferably, the halogen source is hydrogen
25 chloride or molecular chlorine. The contacting with the source of halogen is generally carried out at a temperature greater than 150°C, and preferably, greater than 200°C. The contacting with the source of halogen is usually carried out at a temperature less than 450°C, and preferably, less than 250°C. Typical pressures for the contacting with the source of halogen range from ambient atmospheric pressure to pressures less than 150 psia (1,034
30 kPa).

The dehydrohalogenation process of this invention can be conducted in a reactor of any conventional design suitable, preferably, for gas phase processes, including batch, fixed bed, fluidized bed, transport bed, continuous and intermittent flow reactors. Any process conditions (for example, molar ratios of feed components, temperature, pressure, gas hourly space velocity), can be employed, provided that the desired product alkene or halogenated alkene is selectively obtained. Typically, the process temperature is greater than 100°C, preferably, greater than 150°C, and more preferably, greater than 180°C. Typically, the process temperature is less than 500°C, preferably, less than 300°C, and more preferably, less than 250°C. It is further within the scope of this invention to preheat the reactant feed comprising the halogenated alkane plus optional diluent. Typically, the preheat temperature is greater than 50°C, preferably, greater than 100°C, but typically equal to or less than the process temperature. Preferably, the preheat temperature is less than 500°C, and preferably, less than 300°C. Ordinarily, the process will be conducted at atmospheric pressure or a higher pressure. Typically then, the pressure will be equal to or greater than 14 psia (96 kPa), but typically less than 1,000 psia (6,895 kPa), preferably, less than 600 psia (4,137 kPa), and more preferably, less than 300 psig (2,068 kPa). Typically, the total gas hourly space velocity (GHSV) of the feed (halogenated alkane plus optional diluent) will be greater than 10 ml total feed per ml catalyst per hour (h^{-1}), preferably, greater than 100 h^{-1} , more preferably, greater than 400 h^{-1} . Typically, the total gas hourly space velocity of the feed will be less than 30,000 h^{-1} , preferably, less than 20,000 h^{-1} , and more preferably, less than 10,000 h^{-1} .

The alkene or halogenated alkene formed in the dehydrohalogenation cracking process of this invention may be any alkene or halogenated alkene. Generally, the product alkene contains the same number of carbon atoms as the reactant alkane. Preferably, the alkene or halogenated alkene will be a C_{3-8} , more preferably, a C_{3-4} alkene or halogenated alkene. The halogenated alkene will contain one or more halogen substituents, preferably, selected from chlorine, bromine, and iodine. More preferably, the halogen substituent is chlorine. Non-limiting examples of product alkenes include propylene and butenes, and higher homologues thereof. Non-limiting examples of halogenated alkenes include chloropropenes, dichloropropenes, chlorobutenes, dichlorobutenes, trichlorobutenes, bromopropenes, dibromopropenes, bromobutenes, dibromobutenes. Most preferably, the

alkene is propylene or butene. Most preferably, the halogenated alkene is selected from the group consisting of allyl chloride, 1-chloropropene, 1,3-dichloropropene, and mixtures thereof.

5 1,2-Dichloropropane, which is produced as a substantial by-product in the manufacture of allyl chloride, can be advantageously dehydrohalogenated via the process of this invention selectively to mixtures of allyl chloride and 1-chloropropene, with very low levels of unwanted 2-chloropropene being formed. Generally, in the process of this invention, the conversion of 1,2-dichloropropane is greater than 50 mole percent, and
10 preferably, greater than 60 mole percent at temperatures less than 240°C. For the purposes of this invention, "conversion" is defined as the mole percentage of halogenated alkane feed, such as 1,2-dichloropropane feed, reacted in the dehydrohalogenation process. Typically, the total selectivity to allyl chloride and 1-chloropropene exceeds 90 mole percent. Typically, the selectivity to unwanted 2-chloropropene is less than 2 mole percent,
15 and preferably, less than 1 mole percent. For the purposes of this invention, "selectivity" is defined as the mole percentage of reacted halogenated alkane which forms the specified product.

 The 1-chloropropene, which is produced during dehydrohalogenation of 1,2-
20 dichloropropane, can be advantageously recycled to an allyl chloride reactor, where propylene is chlorinated to allyl chloride. In the reaction environment therein, 1-chloropropene is converted to 1,3-dichloropropene, a component of soil fumigants. From another route, 1,2,3-trichloropropane, produced in the chlorination of allyl chloride, can be selectively dehydrochlorinated by the process of this invention to a mixture comprising
25 predominantly cis and trans-1,3-dichloropropenes. A combined selectivity of greater than 55 mole percent of cis and trans-1,3-dichloro-propenes is typically achieved. Preferably, a combined selectivity of greater than 70 mole percent cis and trans-1,3-dichloropropenes is achieved.

30 One skilled in the art may recognize that the process of this invention cracks hydrogen halide, preferably, hydrogen chloride, from the halogenated alkane feed. The hydrogen halide, which is formed, may be recycled to an oxidative halogenation process,

preferably an oxidative chlorination process, wherein a hydrocarbon or halogenated hydrocarbon (the starting hydrocarbon) can be reacted with oxygen and the recycle hydrogen halide in the presence of an oxidative halogenation catalyst, for example, a copper-based catalyst, to produce a halogenated hydrocarbon having a greater number of halogenated substituents than the starting hydrocarbon. The oxychlorination of ethylene with hydrogen chloride and oxygen to form ethylene dichloride is an example of one such use of the recycle hydrogen chloride stream.

When the dehydrohalogenation catalyst of this process invention is partially or fully deactivated, the catalyst may be easily regenerated. A preferred method of regeneration involves contacting the partially or fully deactivated catalyst with steam at a temperature sufficient to regenerate, at least in part, the catalytic activity. Generally, the steam is provided in a regeneration gas mixture containing an inert diluent, such as nitrogen, helium, or argon. The quantity of steam in the mixture may vary from greater than 0.005 mole percent to less than 50 mole percent, based on the total moles of regeneration gas. Optionally, oxygen may be added to the regeneration gas to aid in the removal of coke. Oxygen-containing mixtures can contain from greater than 1 mole percent to less than 50 mole percent oxygen, as desired; but preferably, the oxygen content of the regeneration gas mixture is greater than 2 mole percent and less than 20 mole percent, based on the total moles of regeneration gas mixture. The regeneration is usually conducted at a temperature greater than 200°C, preferably, greater than 300°C. The regeneration is usually conducted at a temperature less than 700°C, and preferably, less than 600°C. The duration of the regeneration can range from greater than 30 minutes to less than 12 hours, and preferably from greater than 30 minutes to less than 5 hours.

The following examples are provided as an illustration of the process of this invention. These examples should not be construed as limiting the invention in any manner. In light of the disclosure herein, those of skill in the art will recognize alternative embodiments, for example of reactants, process conditions, and catalyst species, which all fall within the scope of this invention. Unless otherwise noted, percentages are given in units of mole percent.

Example 1

A porous lanthanum oxychloride catalyst was prepared as follows. Lanthanum chloride ($\text{LaCl}_3 \cdot 7 \text{H}_2\text{O}$, 15.0 g) was dissolved in deionized water (150 ml). Ammonium hydroxide (6 M, 20 ml) was added to the lanthanum chloride solution quickly with stirring, resulting in a white precipitate. The mixture was centrifuged and the excess liquid decanted yielding a lanthanum-containing gel. The precipitate was calcined at 400°C for 4 hours yielding a porous lanthanum oxychloride catalyst. X-ray diffraction data indicated the presence of a quasi-crystalline form of lanthanum oxychloride. The surface area of the catalyst was $25.8 \text{ m}^2/\text{g}$, as measured by the BET method.

The lanthanum oxychloride (7.35 g , 5 cm^3), prepared hereinabove, was charged into a tubular reactor [nickel base, 1/2 inch (1.25 cm) O.D. x 14 inches (35 cm) length]. The catalyst was dried at 130°C under flowing helium for 1 h and further heated to 230°C under flowing helium. 1,2-Dichloropropane (PDC) was pumped via a Gilson Model 305 pump at a rate of $7.68 \text{ cm}^3/\text{h}$ and mixed with helium at a flow rate of $33 \text{ cm}^3/\text{min}$ to form a PDC/He feed. The feed was preheated to 170°C and fed to the reactor operating at 230°C and atmospheric pressure. The feed gas hourly space velocity was 682 h^{-1} . The composition of the exit feed is shown in Table 1.

Table 1. Dehydrochlorination of 1,2-Dichloropropane (PDC)

Example	1 ^{a,b}	2 ^{a,b}
PDC Conversion	50.22%	65.66%
Sel. 2-Chloropropene	0.46%	0.40%
Sel. cis-1-Chloropropene	54.1%	51.5%
Sel. trans-1-Chloropropene	4.03%	4.47%
Sel. Allyl chloride	37.0%	41.0%

a. PDC Conversion and product selectivities (Sel.) are given in mole percentages.

b. Feed: PDC, $7.68 \text{ cm}^3/\text{h}$, helium, $33 \text{ cm}^3/\text{min}$; 230°C ; atmospheric pressure; feed GHSV, 682 h^{-1} ; feed residence time, 5.3 sec.

From Table 1 it is seen that a lanthanum oxychloride catalyst is capable of dehydrochlorinating 1,2-dichloropropane to cis-1-chloropropene and allyl chloride, both valuable products, in a combined selectivity of over 90 percent. A small amount of trans-1-chloropropene is formed. 2-Chloropropene, which is the least desirable product, is
5 advantageously formed in a selectivity of less than 1 percent.

After 16 h of operation, the PDC conversion had decreased to 31 percent. The catalyst was regenerated by passing a stream of steam at a rate of 1.2 cm³/h and a stream of oxygen and helium (15 percent oxygen in helium) at a rate of 200 cm³/min over the catalyst
10 for 2 h at a temperature of 400°C. After regeneration, the dehydrochlorination process was restarted at the same operating conditions as noted hereinbefore. Start-up conversion of PDC was found to be 40 percent.

Example 2

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A stock solution of lanthanum chloride was prepared by dissolving lanthanum chloride (30.16 g) into deionized and distilled water (18.50 g). The stock solution was used to impregnate alumina (Norton alumina) to incipient wetness at ambient temperature. After drying the impregnated alumina overnight in air at ambient temperature, the alumina-
20 supported lanthanum chloride catalyst was further dried in air at 120°C. The catalyst (10.46 g) was loaded into a reactor and tested in the dehydrochlorination of 1,2-dichloropropane in the manner described in Example 1. Process conditions and results are shown in Table 1, where it is seen that the alumina-supported lanthanum chloride catalyst was capable of dehydrochlorinating 1,2-dichloropropane predominantly to allyl chloride and cis-1-
25 chloropropene, both valuable products, in a combined selectivity of over 90 percent. Only a small amount of trans-1-chloropropene was formed. The least valuable product, 2-chloropropene, was formed in an advantageously small quantity (0.40 percent of the exit stream).

30 After 16 h of operation, the catalyst was regenerated by passing a stream of steam at a rate of 1.2 cm³/h and a stream of oxygen (15 percent in helium) at a rate of 200 cm³/min over the catalyst for 6 h at a temperature of 450°C. After regeneration, the

dehydrochlorination process was restarted at the same operating conditions as noted hereinbefore. The catalyst was found to have regained full activity towards dehydrochlorination.

5 Example 3

The alumina-supported lanthanum chloride catalyst of Example 2 was tested in the dehydrochlorination of "allyl PDC," which is a mixture of halogenated C₃ alkanes and C₃ alkenes obtained as an intermediate cut from an allyl chloride process. More specifically, the "allyl PDC" feed comprises 87.44 percent 1,2-dichloropropane, 7.55 percent 2,3-dichloropropene, 2.02 percent 1,3-dichloropropene, 1.01 percent 3,3-dichloropropene, 0.37 percent allyl chloride, the balance of 1.6 percent being other chlorinated alkanes and alkenes, all percentages given in mole percent. Dehydrochlorination conditions were similar to those used in Example 2. Results are set forth in Table 2 hereinbelow.

Table 2. Dehydrochlorination of "Allyl PDC"^{a,b}

Example	3
PDC Conversion	55.0%
Sel. 2-Chloropropene	0.45%
Sel. cis-1-Chloropropene	51.2%
Sel. trans-1-Chloropropene	5.03%
Sel. Allyl chloride	43.3%

a. "Allyl PDC" comprises, as mole percentages, 87.44 percent 1,2-dichloropropane, 7.55 percent 2,3-dichloropropene, 2.02 percent 1,3-dichloropropene, 1.01 percent 3,3-dichloropropene, 0.37 percent allyl chloride, the balance of 1.6 percent being other chlorinated alkanes and alkenes.

Conversion and product selectivities (Sel.) are given as mole percentages.

b. Feed: "Allyl PDC," 7.68 cm³/h, helium, 33 cm³/min; 230°C; atmospheric pressure; feed GHSV, 682 h⁻¹; residence time, 5.3 sec.

From Table 2 it is seen that the lanthanum chloride catalyst is capable of dehydrochlorinating "Allyl PDC" to a mixture of cis-1-chloropropene and allyl chloride, both valuable products, in a combined selectivity of greater than 90 percent. A small

amount of trans-1-chloropropene is formed. 2-Chloropropene, which is the least desirable product, is advantageously formed in a selectivity of less than 1 percent.

After 16 h of operation, the "Allyl PDC" conversion had decreased to 15 percent.

- 5 The catalyst was regenerated by passing a stream of steam at a rate of 1.2 cm³/h and a stream containing oxygen and helium (15 percent oxygen in helium) at a rate of 200 cm³/min over the catalyst for 2 h at a temperature of 400°C. After regeneration, the dehydrochlorination process was restarted at the same operating conditions as noted hereinbefore. Start-up conversion of PDC was found to be 55 percent.

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Example 4

- The alumina-supported lanthanum chloride catalyst of Example 2 was evaluated in the dehydrochlorination of 1,2,3-trichloropropane. Process conditions were similar to those
15 used in Example 2, with the results set forth in Table 3.

Table 3. Dehydrochlorination of
1,2,3-Trichloropropane (TCP)^{a,b}

Example	4
TCP Conversion	6.1%
Sel. cis-1,3-Dichloropropene	46.7%
Sel. trans-1,3-Dichloropropene	25.5%
Sel. 2,3-Dichloropropene	27.7%

- 20 a. TCP conversion and product selectivities (Sel.) given in mole percentages.
b. Feed: TCP, 7.68 cm³/h, helium, 33 cm³/min; 230°C; atmospheric pressure; feed GHSV, 682 h⁻¹; residence time, 5.3 sec.

- From Table 3 it is seen that the lanthanum chloride catalyst is capable of dehydrochlorinating 1,2,3-trichloropropane predominantly to cis- and trans-1,3-
25 dichloropropenes, which are valuable products, in a combined selectivity of 72.2 percent.

After 16 h of operation, the TCP conversion had decreased to 1.3 percent. The catalyst was regenerated by passing a stream of steam at a rate of 1.2 cm³/h and a stream containing oxygen and helium (15 mole percent oxygen in helium) at a rate of 200 cm³/min

over the catalyst for 2 h at a temperature of 400°C. After regeneration, the dehydrochlorination process was restarted at the same operating conditions as noted hereinbefore. Start-up conversion of TCP was found to be 6.0 percent.

WHAT IS CLAIMED IS:

1. A process of dehydrohalogenating a halogenated alkane to form an alkene or a halogenated alkene, comprising contacting a halogenated alkane having three or more carbon atoms with a rare earth halide or rare earth oxyhalide catalyst under reaction conditions sufficient to prepare the alkene or the halogenated alkene.
2. The process of Claim 1 wherein the halogenated alkane is a chlorinated C₃₋₄ alkane or a mixture of chlorinated C₃₋₄ alkanes.
3. The process of Claim 2, wherein the halogenated alkane is 1,2-dichloropropane or 1,2,3-trichloropropane.
4. The process of Claim 1 wherein the halogenated alkane is a mixture comprising 1,2-dichloropropane and di- and tri-chlorinated C₃ alkanes and C₃ alkenes.
5. The process of Claim 1, wherein a diluent is employed that is nitrogen, helium, argon, carbon monoxide, carbon dioxide, steam, condensable halogenated hydrocarbons or a mixture of one or more of these.
6. The process of any of Claims 1 through 5, wherein the rare earth halide is represented by the formula MX₃, wherein M is at least one rare earth selected from lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium, ytterbium, holmium, terbium, europium, thulium, and lutetium; and wherein X is chloride, bromide, or iodide.
7. The process of Claim 6 wherein M is lanthanum, X is chloride, and the rare earth halide is lanthanum chloride.
8. The process of Claim 6 wherein the rare earth halide is porous with a BET surface area greater than 5 m²/g.

9. The process of Claim 8 wherein the porous rare earth halide has a BET surface area greater than 15 m²/g.
10. The process of Claim 6 wherein the catalyst is deposited on, bonded to, or
5 extruded with a catalyst support or carrier.
11. The process of any of Claims 1 through 5, wherein the rare earth oxyhalide is represented by the formula MOX, wherein M is at least one rare earth lanthanum, cerium, neodymium, praseodymium, dysprosium, samarium, yttrium, gadolinium, erbium,
10 ytterbium, holmium, terbium, europium, thulium and lutetium; and wherein X is chloride, bromide, or iodide.
12. The process of Claim 11 wherein M is lanthanum, X is chloride, and the rare earth oxyhalide is lanthanum oxychloride.
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13. The process of Claim 11 wherein the rare earth oxyhalide is porous and has a BET surface area greater than 12 m²/g.
14. The process of Claim 13 wherein the porous rare earth oxyhalide has a BET
20 surface area greater than 20 m²/g.
15. The process of Claim 11 wherein the catalyst is deposited on, bonded to, or extruded with a catalyst support or carrier.
- 25 16. The process of Claim 1 wherein the catalyst, when partially or fully deactivated, is regenerated by a method comprising contacting the partially or fully deactivated catalyst with a regeneration gas comprising steam under conditions sufficient to regenerate, at least in part, catalytic activity.
- 30 17. The process of Claim 16 wherein the regeneration gas further comprises oxygen.

18. A process of dehydrochlorinating 1,2-dichloropropane to allyl chloride and 1-chloropropene, the process comprising contacting 1,2-dichloropropane with a rare earth halide or rare earth oxyhalide catalyst, the contacting being conducted at a temperature greater than 150°C and less than 500°C, so as to form allyl chloride and 1-chloropropene.

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19. The process of Claim 18 wherein the catalyst is a rare earth chloride or rare earth oxychloride, wherein the rare earth is lanthanum, neodymium, praseodymium, or mixtures thereof.

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20. The process of Claim 19 wherein the rare earth halide is lanthanum chloride or the rare earth oxyhalide is lanthanum oxychloride.

21. The process of any of Claims 18 through 20 wherein the rare earth halide or rare earth oxyhalide is porous.

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22. The process of Claim 21 wherein the porous rare earth halide has a BET surface area greater than 5 m²/g.

23. The process of Claim 21 wherein the porous rare earth oxyhalide has a BET surface area greater than 12 m²/g.

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24. The process of Claim 18 wherein the total selectivity to allyl chloride and 1-chloropropene is greater than 90 mole percent.

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25. The process of Claim 24 wherein 2-chloropropene is produced as a by-product in a selectivity less than 2 mole percent.

26. The process of Claim 18 wherein the 1-chloropropene produced is recycled to an allyl chloride reactor wherein it is chlorinated, and thereafter the chlorinated product is dehydrohalogenated to 1,3-dichloropropene.

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27. The process of Claim 18 wherein the catalyst, when partially or fully deactivated, is regenerated by a method comprising contacting the partially or fully deactivated catalyst with steam, and optionally oxygen, at a temperature greater than 200°C and less than 700°C.

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28. A process of dehydrochlorinating 1,2,3-trichloropropane to form 1,3-dichloropropene, the process comprising contacting 1,2,3-trichloropropane with a rare earth halide or a rare earth oxyhalide catalyst, the contacting being conducted at a temperature greater than 100°C and less than 500°C, so as to form 1,3-dichloropropene.

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29. The process of Claim 28 wherein the catalyst is a rare earth chloride or rare earth oxychloride, wherein the rare earth is lanthanum, neodymium, praseodymium, or mixtures thereof.

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30. The process of Claim 29 wherein the rare earth halide is lanthanum chloride, and the rare earth oxyhalide is lanthanum oxychloride.

31. The process of Claim 30 wherein the rare earth halide or rare earth oxyhalide is porous.

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32. The process of Claim 31 wherein the porous rare earth halide has a BET surface area greater than 5 m²/g.

33. The process of Claim 31 wherein the porous rare earth oxyhalide has a BET surface area greater than 12 m²/g.

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34. The process of Claim 28 wherein the catalyst, when partially or fully deactivated, is regenerated by a method comprising contacting the partially or fully deactivated catalyst with steam, and optionally oxygen, at a temperature greater than 200°C and less than 700°C.

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 00/31488

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C17/25 C07C21/04 C07C21/067 C07C21/073 C07C1/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 945 573 A (NAPPA MARIO JOSEPH ET AL) 31 August 1999 (1999-08-31) claims 1,11	1
Y	US 3 927 131 A (WARD JOE ARTHUR) 16 December 1975 (1975-12-16) the whole document	1-3,6,7, 10,18,28
Y	US 5 008 225 A (MAGISTRO ANGELO J) 16 April 1991 (1991-04-16) the whole document	1-3,6,7, 10,18,28
Y	EP 0 372 183 A (SUMITOMO CHEMICAL CO) 13 June 1990 (1990-06-13) page 2, line 23 - line 29; claim 1	1-3,6,7, 10,18,28

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

11 April 2001

Date of mailing of the international search report

25/04/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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